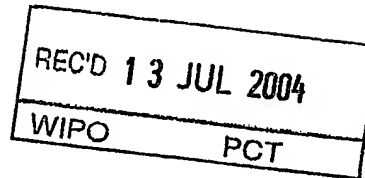




INVESTOR IN PEOPLE

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Dated

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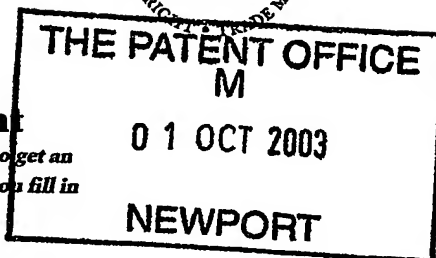


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P01/7700 000-0322963.0

1/77

# Request for grant of a patent

(See the notes on the back of this form. You can also get an explanatory leaflet from the Patent Office to help you fill in this form)



The Patent Office

Cardiff Road  
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NP10 8QQ

1. Your reference

AA 1676 GB

2. Patent application number

(The Patent Office will fill in this part)

0322963.0

23 JUN 2003

3. Full name, address and postcode of the or of each applicant (underline all surnames)

JOHNSON MATTHEY PUBLIC LIMITED COMPANY  
2-4 COCKSPUR STREET  
TRAFALGAR SQUARE  
LONDON SW1 5BQ

Patents ADP number (if you know it)

If the applicant is a corporate body, give the country/state of its incorporation

GB 536 268 007

4. Title of the invention

METHODS OF CONTROLLING REDUCANT  
ADDITION

5. Name of your agent (if you have one)

ANDREW DOMINIC NUNN

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

JOHNSON MATTHEY TECHNOLOGY CENTRE  
BLOUNTS COURT  
SONNING COMMON  
READING RG4 9NH

Patents ADP number (if you know it)

3991411501

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and (if you know it) the or each application number

Country

Priority application number  
(if you know it)

Date of filing  
(day / month / year)

GB

0314463.1

23 JUNE 2003

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application

Date of filing  
(day / month / year)

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? (Answer 'Yes' if:

YES

- a) any applicant named in part 3 is not an inventor, or
  - b) there is an inventor who is not named as an applicant, or
  - c) any named applicant is a corporate body.
- See note (d))

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Continuation sheets of this form

Description

Claim(s)

Abstract

Drawing(s)

0

7

3

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10. If you are also filing any of the following, state how many against each item.

Priority documents

Translations of priority documents

Statement of inventorship and right to grant of a patent (*Patents Form 7/77*)

Request for preliminary examination and search (*Patents Form 9/77*)

Request for substantive examination (*Patents Form 10/77*)

Any other documents  
(*please specify*)

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11.

I/We request the grant of a patent on the basis of this application.

Signature

*J. W. Wishart*  
I C WISHART

Date

30 Sep 03

12. Name and daytime telephone number of person to contact in the United Kingdom

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## METHODS OF CONTROLLING REDUCANT ADDITION

The present invention relates to methods of controlling reductant addition to catalytically convert  $\text{NO}_x$  in exhaust gas of an internal combustion engine to  $\text{N}_2$ .

5

It is known to catalytically reduce  $\text{NO}_x$  in exhaust gas of an internal combustion engine to  $\text{N}_2$  with a suitable reductant. Three examples are selective catalytic reduction (SCR), lean- $\text{NO}_x$  catalysis and  $\text{NO}_x$ -trap regeneration.

10

In SCR, the reductant is typically a  $\text{NO}_x$ -specific reactant. By " $\text{NO}_x$  specific reactant" herein, we mean a reducing agent that, in most conditions, preferentially reduces  $\text{NO}_x$  over other components of a gaseous mixture. Examples of  $\text{NO}_x$ -specific reactants include nitrogenous compounds such as nitrogen hydrides, e.g. ammonia ( $\text{NH}_3$ ) or hydrazine, or an  $\text{NH}_3$  precursor.

15

By " $\text{NH}_3$  precursor" we mean one or more compounds from which  $\text{NH}_3$  can be derived, e.g. by hydrolysis. These include urea ( $\text{CO}(\text{NH}_2)_2$ ) as an aqueous solution or as a solid or ammonium carbamate ( $\text{NH}_2\text{COONH}_4$ ). If the urea is used as an aqueous solution, a eutectic mixture, e.g. 32.5% urea (aq), is preferred. Additives can be included

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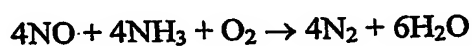
in the aqueous solutions to reduce the crystallisation temperature.

25

Known SCR catalysts include Pt-based catalysts, which can catalyse the reduction of  $\text{NO}_x$  with  $\text{NH}_3$  at between about  $175^\circ\text{C}$  and about  $250^\circ\text{C}$ , medium temperature vanadium-based catalysts e.g.  $\text{V}_2\text{O}_5/\text{TiO}_2$ , which operate in the temperature range between about  $260^\circ\text{C}$  and about  $450^\circ\text{C}$  and zeolite-based catalysts which function with increasing activity at increasing temperature.

30

Several chemical reactions occur in the  $\text{NH}_3$  SCR system, all of which represent desirable reactions which reduce  $\text{NO}_x$  to elemental nitrogen. The dominant reaction mechanism is represented in equation (1).



(1)

Competing, non-selective reactions with oxygen can produce secondary emissions or may unproductively consume  $\text{NH}_3$ . One such non-selective reaction is the complete oxidation of  $\text{NH}_3$ , represented in equation (2).



Urea hydrolyses at temperatures above  $160^\circ\text{C}$  according to equation (3) to liberate  $\text{NH}_3$  itself. It also thermally decomposes at this temperature and above according to equations (4) and (5) resulting in reduction of  $\text{NO}_x$ .

10



15            It will be appreciated that at lower temperatures, below about  $100\text{-}200^\circ\text{C}$ ,  $\text{NH}_3$  can also react with  $\text{NO}_2$  to produce explosive mixture of ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ) and ammonium nitrite ( $\text{NH}_4\text{NO}_2$ ) according to equation (6).



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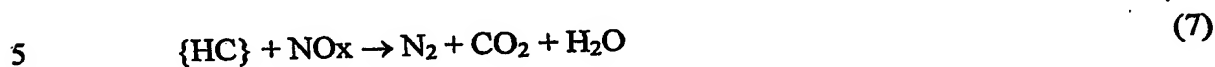
For the avoidance of doubt, the present invention does not embrace such reactions or the promotion of conditions which bring them about. For example, the reaction can be avoided by ensuring that the temperature does not fall below about  $200^\circ\text{C}$  or by supplying into a gas stream less than the precise amount of  $\text{NH}_3$  necessary for the stoichiometric reaction with  $\text{NO}_x$  (1 to 1 mole ratio).

25

Lean- $\text{NO}_x$  catalysts (LNCs) are sometimes also referred to in the literature as non-selective catalytic reduction (NSCR) catalysts, hydrocarbon selective catalytic reduction (HC-SCR) catalysts, lean- $\text{NO}_x$  reduction catalysts, "De $\text{NO}_x$  catalysts" and

30  $\text{NO}_x$  occluding catalysts.

In lean- $\text{NO}_x$  catalysis, hydrocarbons (HC) react with nitrogen oxides ( $\text{NO}_x$ ), rather than oxygen ( $\text{O}_2$ ), to form nitrogen ( $\text{N}_2$ ), carbon dioxide ( $\text{CO}_2$ ) and water ( $\text{H}_2\text{O}$ ) according to equation (7).



The competitive, non-selective reaction with oxygen is given by Equation (8).



There are two preferred groups of LNC to selectively promote the desired reaction (7) described in the literature: platinum (Pt) on alumina ( $\text{Al}_2\text{O}_3$ ) and copper (Cu)-substituted zeolite such as Cu/ZSM-5.

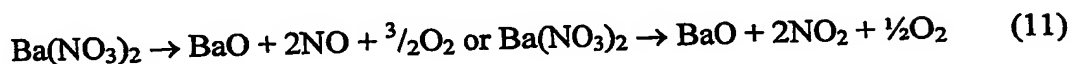
A typical  $\text{NO}_x$ -trap formulation includes a catalytic oxidation component, such as platinum, a  $\text{NO}_x$ -storage component, such as compounds of alkali metals e.g. potassium and/or caesium; compounds of alkaline earth metals, such as barium or strontium; and compounds of rare-earth metals, typically lanthanum and/or yttrium; and a reduction catalyst, e.g. rhodium. One mechanism commonly given for  $\text{NO}_x$ -storage during lean engine operation for this formulation is set out in equation (9) and (10) using barium as an illustrative Example.



In step (9), the nitric oxide reacts with oxygen on active oxidation sites on the platinum to form  $\text{NO}_2$ . The second step involves adsorption of the  $\text{NO}_2$  by the storage material in the form of an inorganic nitrate.

When the engine runs intermittently under rich conditions or at elevated temperatures, the nitrate species become thermodynamically unstable and decompose, producing NO or  $\text{NO}_2$  according to equation (11) below. Under rich conditions, these

nitrogen oxides are subsequently reduced by carbon monoxide, hydrogen and hydrocarbons to  $N_2$ , which can take place over the reduction catalyst.



In the reactions of (9)-(12) above, the reactive barium species is given as the oxide. However, it is understood that in the presence of air or exhaust gas containing  $CO_2$  and  $H_2O$  the barium may also be in the form of the carbonate or possibly the hydroxide. The above reaction schemes can be adapted accordingly for species of barium other than the oxide. We also explain in our WO 00/21647 that  $NO_x$ -specific reactants can be used to regenerate a  $NO_x$ -trap.

A problem with the above  $NO_x$  reduction methods is to control the addition of the reductant. If too little reductant is added,  $NO_x$  reduction may be inadequate to meet an emission standard. If too much reductant is added this can cause a number of problems. For example, if the reductant is ammonia, its release into the atmosphere is undesirable because it is a biological poison and it has an unpleasant odour. Whilst excess ammonia can be oxidised using a suitable catalyst downstream of the  $NO_x$ -reduction catalyst, this produces  $NO_x$ , thus defeating the very purpose of the  $NO_x$  reduction method. Hydrocarbon fuels, e.g. diesel or gasoline, are also legislated components of exhaust gas and so emission of excess hydrocarbon reductant can cause the system to fail a relevant emission standard.

Systems to control reductant addition are known, but tend to require very complicated control regimes involving multiple sensor inputs and processors to run complex algorithms. As a result, such systems are very expensive.

We have investigated methods of calibrating reductant addition and of controlling reductant addition by feedback. We have now devised a number of simple methods and systems that are cheap and effective at reducing reductant-based emissions. Systems embodying these methods are particularly relevant to the retrofit market.

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A first aspect of the invention makes use of only a single temperature measurement, e.g. using a thermocouple, as the control input. Preferably, no reductant is added below a pre-determined temperature because the temperature is too low for the complete  $\text{NO}_x$  removal reaction to take place. As the load on an engine is increased, the  $\text{NO}_x$  level in the exhaust gas increases in a roughly linear fashion. Similarly, the exhaust gas temperature increases with load. We expect, therefore, that for a given engine in a particular application there is a relationship between  $\text{NO}_x$  content in the exhaust gas and its temperature. And, that this may approximate to a linear relationship. So, in its simplest form, in this aspect of the invention, the rate of reductant introduced is proportional to the temperature of the exhaust gas. Addition of a reductant in this way provides a very efficient and simple way of maintaining  $\text{NO}_x$  reduction on a vehicle. The actual amount of reductant added at different exhaust gas temperatures can depend on the nature of the specific application. But, there may be a trend for more reductant to be needed to remove larger amounts of  $\text{NO}_x$  at higher temperatures. In practice a calibration process would determine the exact amounts.

In a system embodiment of the first aspect, the invention provides an exhaust system for an internal combustion engine, which system comprising a catalyst for reducing  $\text{NO}_x$  in exhaust gas to  $\text{N}_2$  with a suitable reductant, a source of reductant, means for contacting the catalyst with the reductant, means for sensing the temperature of the exhaust gas and/or the catalyst bed and means, when in use, for controlling reductant addition, wherein the reductant addition control means supplies an amount of reductant to the catalyst corresponding to a measured temperature value of the exhaust gas and/or catalyst bed, which temperature value has been pre-determined to correlate, in use, with an amount of  $\text{NO}_x$  in the exhaust gas.

In a method embodiment of the first aspect, the invention provides a method of calibrating an amount of reductant addition required to reduce  $\text{NO}_x$  in an exhaust gas of an internal combustion engine to  $\text{N}_2$  over a suitable catalyst, which method comprising measuring  $\text{NO}_x$  in the exhaust gas at a plurality of exhaust gas and/or catalyst bed temperatures and correlating each exhaust gas and/or catalyst bed temperature value with an amount of reductant addition required to reduce the  $\text{NO}_x$  over the catalyst.



A second aspect of the invention provides a simple means of controlling reductant addition by feedback in real-time. In the second aspect, an oxidation catalyst is disposed downstream of the  $\text{NO}_x$  removal catalyst which is contacted with a reductant. The system is arranged so that the gas is always lean over the oxidation catalyst, e.g. by using secondary addition of air if required. As in the first aspect described above, desirably no reductant is added below a certain critical exhaust gas temperature, at which  $\text{NO}_x$  reduction is ineffective. Above this temperature, increasing the amount of reductant causes increasing amounts of  $\text{NO}_x$  in the exhaust gas to be reduced. In practice there is a limit to this effect, and then introducing more reductant fails to enhance  $\text{NO}_x$  reduction. So, there is a region of small excess reductant slip from the  $\text{NO}_x$  reduction catalyst that corresponds to a desirable addition rate above which any more reductant is wasted.

Because the overall gas composition is arranged to be lean, any excess reductant can be oxidised over the downstream oxidation catalyst, and the resulting exotherm may result in a temperature increase across the oxidation catalyst. The inlet temperature to the oxidation catalyst may vary considerably during use, but in this method we are concerned only with the  $\Delta T$  that is a measurement of the excess reductant present. The control strategy is based in adjusting the rate of reductant addition to keep the measured  $\Delta T$  within a pre-determined range corresponding to an optimum  $\text{NO}_x$  removal: reductant addition is increased if  $\Delta T$  is too small, or decreased if  $\Delta T$  is larger than desired for optimum efficient  $\text{NO}_x$  conversion.

According to a system embodiment of the second aspect of the invention, there is provided an exhaust system for an internal combustion engine, which system comprising a catalyst for reducing  $\text{NO}_x$  in an exhaust gas to  $\text{N}_2$  with a suitable reductant, a source of reductant, means for contacting the catalyst with the reductant, an oxidation catalyst disposed downstream of the  $\text{NO}_x$  reduction catalyst, means for determining a temperature difference ( $\Delta T$ ) across the oxidation catalyst and means, when in use, for controlling reductant addition, wherein the reductant addition control means controls a rate of reductant addition to maintain  $\Delta T$  within a pre-determined range, wherein the system is configured so that the exhaust gas composition over the oxidation catalyst is lean.

In a method embodiment of the second aspect of the invention, a method of controlling, by feedback, addition of reductant to a catalyst suitable for reducing  $\text{NO}_x$  in an exhaust gas of an internal combustion engine to  $\text{N}_2$  with the reductant comprises providing an oxidation catalyst for oxidising the reductant downstream of the  $\text{NO}_x$  reduction catalyst, measuring the exhaust gas temperature upstream of the oxidation catalyst, measuring the exhaust gas temperature downstream of the oxidation catalyst, determining the difference between the inlet and the outlet temperatures ( $\Delta T$ ) and adjusting reductant addition so that  $\Delta T$  is within a pre-determined range.

10 The internal combustion engine can be a diesel or lean-burn gasoline engine, such as a gasoline direct injection engine. The diesel engine can be a light duty engine or a heavy-duty engine, as defined by the relevant legislation.

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**CLAIMS:**

1. An exhaust system for an internal combustion engine, which system comprising a catalyst for reducing  $\text{NO}_x$  in exhaust gas to  $\text{N}_2$  with a suitable reductant, a source of  
5 reductant, means for contacting the catalyst with the reductant, means for sensing the temperature of the exhaust gas and/or the catalyst bed and means, when in use, for controlling reductant addition, wherein the reductant addition control means supplies an amount of reductant to the catalyst corresponding to a measured temperature value of the exhaust gas and/or catalyst bed, which temperature value has been pre-determined to  
10 correlate, in use, with an amount of  $\text{NO}_x$  in the exhaust gas.
2. A method of calibrating an amount of reductant addition required to reduce  $\text{NO}_x$  in an exhaust gas of an internal combustion engine to  $\text{N}_2$  over a suitable catalyst, which method comprising measuring  $\text{NO}_x$  in the exhaust gas at a plurality of exhaust gas and/or  
15 catalyst bed temperatures and correlating each exhaust gas and/or catalyst bed temperature point with an amount of reductant addition required to reduce the  $\text{NO}_x$  over the catalyst.
3. An exhaust system for an internal combustion engine, which system comprising a  
20 catalyst for reducing  $\text{NO}_x$  in exhaust gas to  $\text{N}_2$  with a suitable reductant, a source of reductant, means for contacting the catalyst with the reductant, an oxidation catalyst disposed downstream of the  $\text{NO}_x$  reduction catalyst, means for determining a temperature difference ( $\Delta T$ ) across the oxidation catalyst and means, when in use, for  
controlling reductant addition, wherein the reductant addition control means controls a  
25 rate of reductant addition to maintain  $\Delta T$  within a pre-determined range, wherein the system is configured so that the exhaust gas composition over the oxidation catalyst is lean.
4. A method of controlling, by feedback, addition of reductant to a catalyst suitable  
30 for reducing  $\text{NO}_x$  in an exhaust gas of an internal combustion engine to  $\text{N}_2$  with the reductant, which method comprising providing an oxidation catalyst for oxidising the reductant downstream of the  $\text{NO}_x$  reduction catalyst, measuring the exhaust gas temperature upstream of the oxidation catalyst, measuring the exhaust gas temperature

downstream of the oxidation catalyst, determining the difference between the inlet and the outlet temperatures ( $\Delta T$ ) and adjusting reductant addition so that  $\Delta T$  is within a pre-determined range.

- 5 5. An exhaust system according to claim 1 or 3, wherein reductant addition is suspended when the exhaust gas and/or the catalyst bed temperature is below a pre-determined temperature.
6. An exhaust system according to claim 1, 3 or 5, wherein reductant addition is  
10 suspended when the exhaust gas and/or the catalyst bed temperature is above a pre-determined temperature.
7. A method according to claim 2 or 4, wherein reductant addition is suspended  
15 when the exhaust gas and/or the catalyst bed temperature is below a pre-determined temperature.
8. A method according to claim 2, 4 or 7, wherein reductant addition is suspended  
when the exhaust gas and/or the catalyst bed temperature is above a pre-determined  
20 temperature.
9. An exhaust system according to claim 3, wherein the rate of reductant addition is  
decreased if  $\Delta T$  is too large.
10. A method according to claim 4, wherein the rate of reductant addition is  
25 decreased if  $\Delta T$  is too large.
11. An exhaust system according to claim 1, 3, 5, 6 or 9, wherein the reductant is a hydrocarbon and the catalyst is a lean- $\text{NO}_x$  catalyst.
- 30 12. An exhaust system according to claim 1, 3, 5, 6 or 9, wherein the reductant is a  $\text{NO}_x$ -specific reactant and the catalyst is a selective catalytic reduction (SCR) catalyst.

13. An exhaust system according to claim 11 or 12, wherein the catalyst comprises a NO<sub>x</sub>-absorbent.
14. A method according to claim 2, 4, 7, 8 or 10, wherein the reductant is a hydrocarbon and the catalyst is a lean-NO<sub>x</sub> catalyst.
15. A method according to claim 2, 4, 7, 8 or 10, wherein the reductant is a NO<sub>x</sub>-specific reactant and the catalyst is a selective catalytic reduction (SCR) catalyst.
16. A method according to claim 14 or 15, wherein the catalyst comprises a NO<sub>x</sub>-absorbent.

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